

US EPA ARCHIVE DOCUMENT

SESSION 3

Corrective Measures Selection Process

REMEDIAL TECHNOLOGIES OVERVIEW



Remedial Technologies Sources

- ▶ Federal Remedial Technologies Roundtable: www.frtr.gov
 - Treatment Technologies Screening Matrix included in references
- ▶ Hazardous Waste Clean-Up Information (CLU-IN): www.clu-in.org
- ▶ Ground-Water Remediation Technologies Analysis Center (GWRTAC): www.gwrtac.org
- ▶ EPA Remediation/Cleanup Technologies (focused on USTs): www.epa.gov/swerust1/cat/remedial.htm



Agenda: Remedial Technologies Overview

- ▶ Evaluating Groundwater Remediation Options
 - Ex-situ treatment processes
 - In-situ treatment processes

- ▶ Evaluating Soil Remediation Options
 - Ex-situ treatment processes
 - In-situ treatment processes



Evaluating Groundwater Remediation Options



Evaluating Groundwater Remediation Options

- ▶ The best method of a response action for a situation should be contemplated from the very start of the RFI process
 - Decision process should not be in a vacuum until the end of the RFI process
 - Experience with sites will assist in developing better presumptive remedies for cleanup methods for sites

- ▶ Proper site characterization data of site geology are essential to understanding and to effectively remediating contaminated groundwater:
 - Type of aquifer
 - Hydraulic properties
 - Groundwater flow characteristics
 - Contaminants



Type of Aquifer

- ▶ The evaluation of the type of aquifer will provide information on the potential transmissivity of contaminants in groundwater
 - Confining layer
 - Thickness
 - Extent
 - Conductivity
 - Complexity of system
 - Fractured rock system

Hydraulic Properties

- ▶ Hydraulic properties describe the factors that impact the movement of groundwater
 - Hydraulic conductivity
 - Porosity/effective porosity
 - Groundwater flow rates
 - Hydraulic gradient

Groundwater and Flow Characteristics

- ▶ The amount of groundwater and the direction of flow are important factors in addressing potential remedial technologies applicable to a site
 - Recharge/discharge zones
 - Groundwater flow directions
 - Groundwater contour maps
 - Acidity
 - Hardness

Contaminant Characteristics

- ▶ Basic information on contaminants provides information on the potential mobility of the contaminant within the groundwater medium
 - Solubility (relative to pH, temperature, DNAPL)
 - Volatility
 - Adsorptive retardation properties
 - Absorptive retardation properties
 - Degradation properties
 - Toxicity

Ex-situ Groundwater Treatment Processes



Pump-and-Treat Technology

- ▶ Pump-and-treat is the most common form of groundwater remediation
- ▶ Involves removing contaminated groundwater from the subsurface, treating it to remove the contaminants, and discharging the treated water

Pump-and-Treat Technology

- ▶ Basic components of pump-and-treat are:
 - Extraction wells
 - Pumping and piping systems
 - Water treatment system
 - Treated water monitoring
 - Groundwater monitoring network

Pump-and-Treat Technology



Pump-and-Treat Technology

- ▶ What pump-and-treat can do well:
 - Provide hydraulic control to minimize spreading (mitigation)
 - Redirect contaminant plume to protect potential receptors
 - Contaminant removal (contaminant/aquifer dependent)

Pump-and-Treat Technology

- ▶ Considerations
 - Aquifer properties
 - Contaminants
 - Types of contaminants
 - Properties of contaminants
 - Extent of contamination
 - Goals
 - Project duration
 - Cost

Pump-and-Treat Technology

- ▶ Considerations (cont.)

- Aquifer properties

- $Q = -KA \, dh/dl$ (Darcy's law – specific discharge)

- Q = volumetric flow rate (m^3/s or ft^3/s)

- A = flow area perpendicular to L (m^2 or ft^2)

- K = hydraulic conductivity (m/s or ft/s)

- dh = change in hydraulic head (m or ft)

- dl = change in flow path length (m or ft)

- (e.g., geology, hydraulic conductivity, potentiometric surface)

- Outside hydraulic control

- (e.g., wells, surface water discharge, drought)

Pump-and-Treat Technology

- ▶ Examples of groundwater treatment technologies used in pump-and-treat:
 - Air stripping
 - Carbon adsorption
 - Precipitation
 - Chemical oxidation
 - Bioreactors

Pump-and-Treat Technology - Limitations

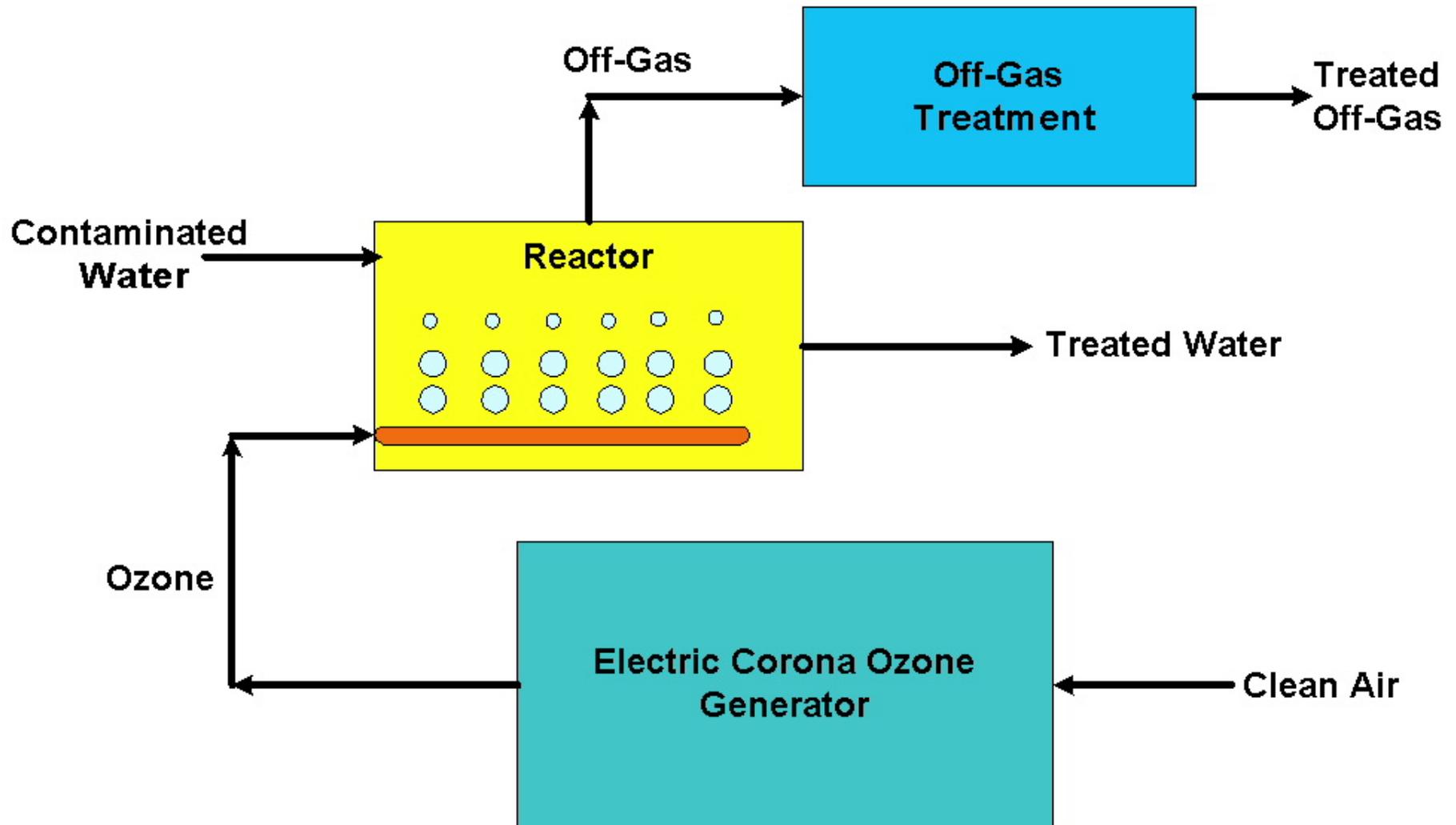
- ▶ Pump-and-treat systems often take a long time to meet cleanup goals
- ▶ Radial influence
- ▶ “Rebound” effect
- ▶ Treated groundwater disposal pathway (discharge or inject)



Ex-Situ Chemical Oxidation (organics)

- ▶ Involves mixing an oxidizing agent with contaminated groundwater
- ▶ Oxidizing agents include:
 - Sodium hypochlorite (or other hypochlorite compounds)
 - Hydrogen peroxide
 - Chlorine
 - Chlorine dioxide
 - Potassium permanganate
 - Ozone
- ▶ The oxidation process mineralizes most organic compounds to carbon dioxide, water, and salts

Ex-Situ Chemical Oxidation (organics)



Applicability

- ▶ Ex-situ chemical oxidation is typically used to treat water residual from a primary treatment process

- ▶ Can be used to treat:
 - VOCs and SVOCs
 - Pesticides
 - Ordnance
 - PCBs

Limitations

- ▶ Incomplete oxidation and intermediate contaminants may form depending on the contaminants and oxidizing agents used
- ▶ Often not cost-effective for highly contaminated sites due to the large amounts of oxidizing agents required
- ▶ Chlorinated oxidizing agents may form daughter products such as chloromethanes

Cost

- ▶ The typical cost for ex-situ chemical oxidation (organics) averages \$ 0.35 - \$ 2.00 per 1,000 gallons

Other Chemical Oxidation Technologies

- ▶ Chemical Oxidation/Ultraviolet Light Oxidation
- ▶ Chemical Reduction/Oxidation (for inorganics)

In-situ Groundwater Treatment Processes



Monitored Natural Attenuation (MNA)

- ▶ Consider contaminant properties and site characteristics
- ▶ Physical and chemical properties of contaminants
 - Aqueous solubility
 - Sorption coefficients (K_{oc} , K_{ow})
 - Chemical stability
 - Biological transformation processes and rates
 - Aerobic or anaerobic
 - Heterotrophic or autotrophic

MNA – Hydrogeologic Evaluation

- ▶ Hydrogeologic setting controls contaminant migration rates and impacts physical, chemical, and biological processes
- ▶ Spatial distribution of hydraulic properties also effects subsurface processes
 - Well-sorted sands and gravels – less variable, high flow velocities
 - Interbedded clays – slower migration rates, adsorb/retard contaminants
 - Fractured rock settings – added complexity

MNA – Site Geochemistry

- ▶ pH
- ▶ Redox conditions
- ▶ Cation/anion chemistry of groundwater
- ▶ Organic carbon availability – natural and contaminant sources
- ▶ Compare contaminated and clean areas
- ▶ Concentrations of degradation products

MNA Synthesis – Contamination and Hydrogeology

- ▶ Compare contaminant physical and chemical properties with site characteristics
- ▶ Site chemistry compatibility with transformation processes
- ▶ Presence and status of secondary sources
- ▶ Waste/source properties
- ▶ Toxicity and mobility of transformation products

MNA – Processes and Contaminant Types

<u>Contaminant</u>	<u>Processes</u>	<u>Considerations</u>
Chlorinated solvents	Reductive dechlorination, aerobic degradation	Redox conditions, DNAPL, groundwater concentrations, degradation products, carbon sources
Petroleum Hydrocarbons	Aerobic degradation	Redox conditions, LNAPL control, O ₂
Metals	Adsorption, chemical precipitation	pH, alkalinity, concentrations, complexing agents, clay content of aquifer

MNA – Processes and Contaminant Types (cont.)

<u>Contaminant</u>	<u>Processes</u>	<u>Considerations</u>
Non-metals	Adsorption, chemical precipitation	pH, redox, alkalinity, As, Se most important
Herbicides/ Pesticides	Adsorption, aerobic degradation, anaerobic degradation, hydrolysis	Consider individual degradation processes, toxicity/mobility of degradation products
Polycyclic Aromatic Hydrocarbons	Adsorption, aerobic degradation, anaerobic degradation	Clay and organic carbon content of aquifer, presence of solvents

MNA – Regulatory and Implementation Issues

- ▶ Guidance provided in EPA's MNA directive:
<http://www.epa.gov/OUST/directiv/d9200417.pdf>
- ▶ Use data and modeling to estimate maximum extent of contamination
- ▶ Evaluate exposure potentials and availability of administrative controls
- ▶ In general, where degradation rates are greater than migration rates, plume extent will be stable or decreasing

Bioremediation

- ▶ Anaerobic and aerobic processes may be important
- ▶ In-situ bioremediation can be enhanced
- ▶ Contaminant types and site chemical conditions are important factors for assessing bioremediation potential

Bioremediation Process Types – Aerobic

- ▶ Most common bioremediation is sparging
- ▶ Sparging provides oxygen to subsurface at much greater rate than natural transport processes
- ▶ Compounds amenable to aerobic degradation are mainly small molecule petroleum hydrocarbons
 - Consider aquatic fate process data

Bioremediation Process Types – Anaerobic

- ▶ May be important for a variety of organic compounds
- ▶ In naturally reducing conditions, addition of nutrients and substrate may promote degradation
- ▶ Reduction of ferric iron may be an important co-metabolic process

Bioremediation – Additive Types

- ▶ Bioremediation can be enhanced by addition of agents
- ▶ Oxygen addition is achieved by sparging or addition of compounds
- ▶ Anaerobic remediation can be enhanced by addition of hydrogen releasing compounds
- ▶ Nutrient addition and substrate addition can be achieved by injection
- ▶ Organism addition has not been practical



Bioremediation – Suitability of Site Conditions



Organic Clays:
Reducing Conditions

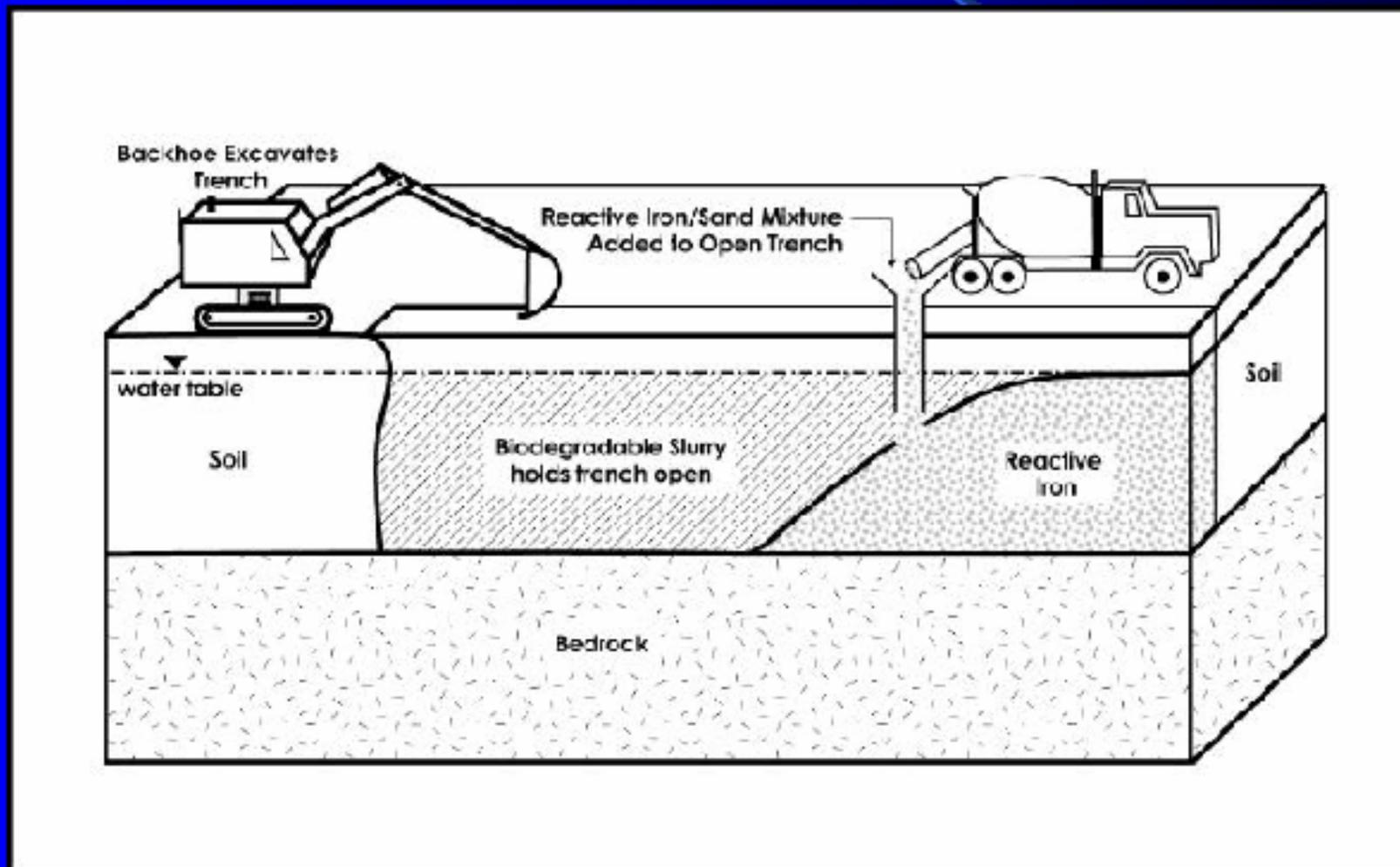


Permeable Sandstone:
Oxidizing Conditions

Permeable Reactive Barriers

- ▶ Installed by trenching and placing permeable reactive material in the subsurface
- ▶ Geometry of aquifer and flow directions must be considered
- ▶ Requires skill and experience to implement in the field

Permeable Reactive Barriers – Installation



Permeable Reactive Barriers – Types and Uses

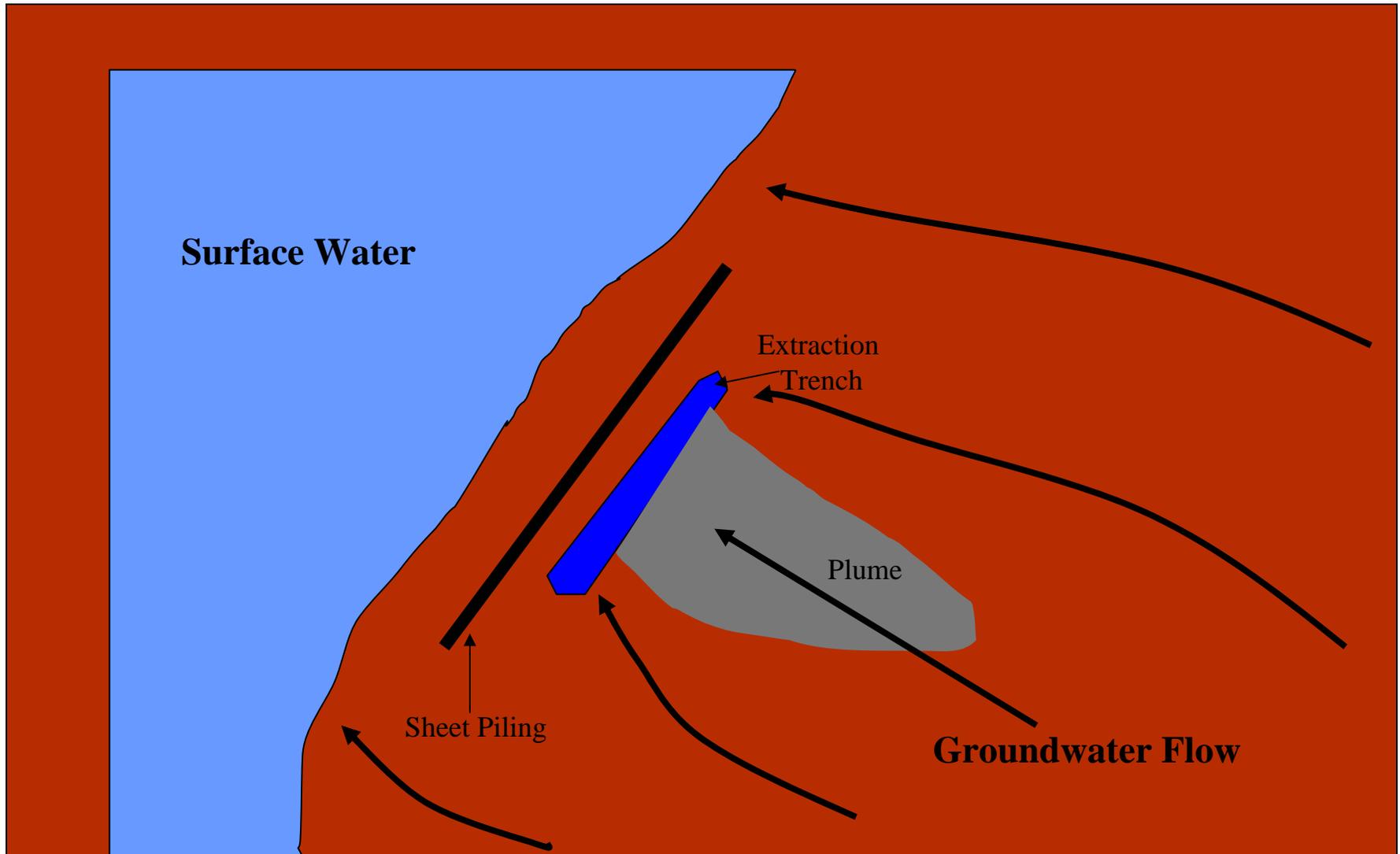
- ▶ Most common type is reactive iron
- ▶ Granular activated carbon or charcoal may be used for organic compounds
- ▶ Low maintenance, but some maintenance may be required
- ▶ Can be used in combination with impermeable barriers in “gate and channel” configurations



Physical Barriers: Slurry Walls and Sheet Piling

- ▶ Useful in certain situations, especially shallow contamination with limited areal extent
- ▶ Often a component of hydraulic control as part of active remediation
- ▶ Consider changes induced in the in-flow system

Physical Barriers – Example Sheet Piling



Evaluating Soil Remediation Options



Evaluating Soil Remediation Options

- ▶ Proper site characterization data of site geology are essential to understanding and to effectively remediating contaminated soil:
 - Porosity (total and effective)
 - Conductivity
 - Moisture content
 - Organic carbon
 - Content
 - Cation and anion exchange capacity
 - Grain-size distribution



Ex-situ Soil Treatment Processes



Excavation and Land Disposal



Excavation

- ▶ Excavation is a relatively simple process of removing contaminated surface and subsurface materials from hazardous waste sites using standard construction practices
- ▶ Excavation is effective but very labor intensive
 - Partially automated pond sludge removal, radioactive waste handling, and surveying equipment are in use
 - Prior to 1984, excavation and off-site disposal were the most common method for cleaning up hazardous waste sites
- ▶ Excavation is not a stand-alone treatment technology but the initial step for all ex-situ treatment processes



Excavation

- ▶ Contaminated material is typically removed in lifts where intermediate sampling can be conducted to confirm the depth of contamination

- ▶ Contaminated material is transported to treatment and/or disposal facilities (on or off site)

- ▶ Some treatment of the waste or contaminated media usually is required to meet land disposal restrictions, which can include:
 - Acid-base neutralization
 - Solidification
 - Hypochlorite oxidation
 - Flash point reduction
 - Removal of free liquids by addition of soil, lime, fly ash, or polymers



Excavation Equipment

▶ Bulldozer



▶ Excavator

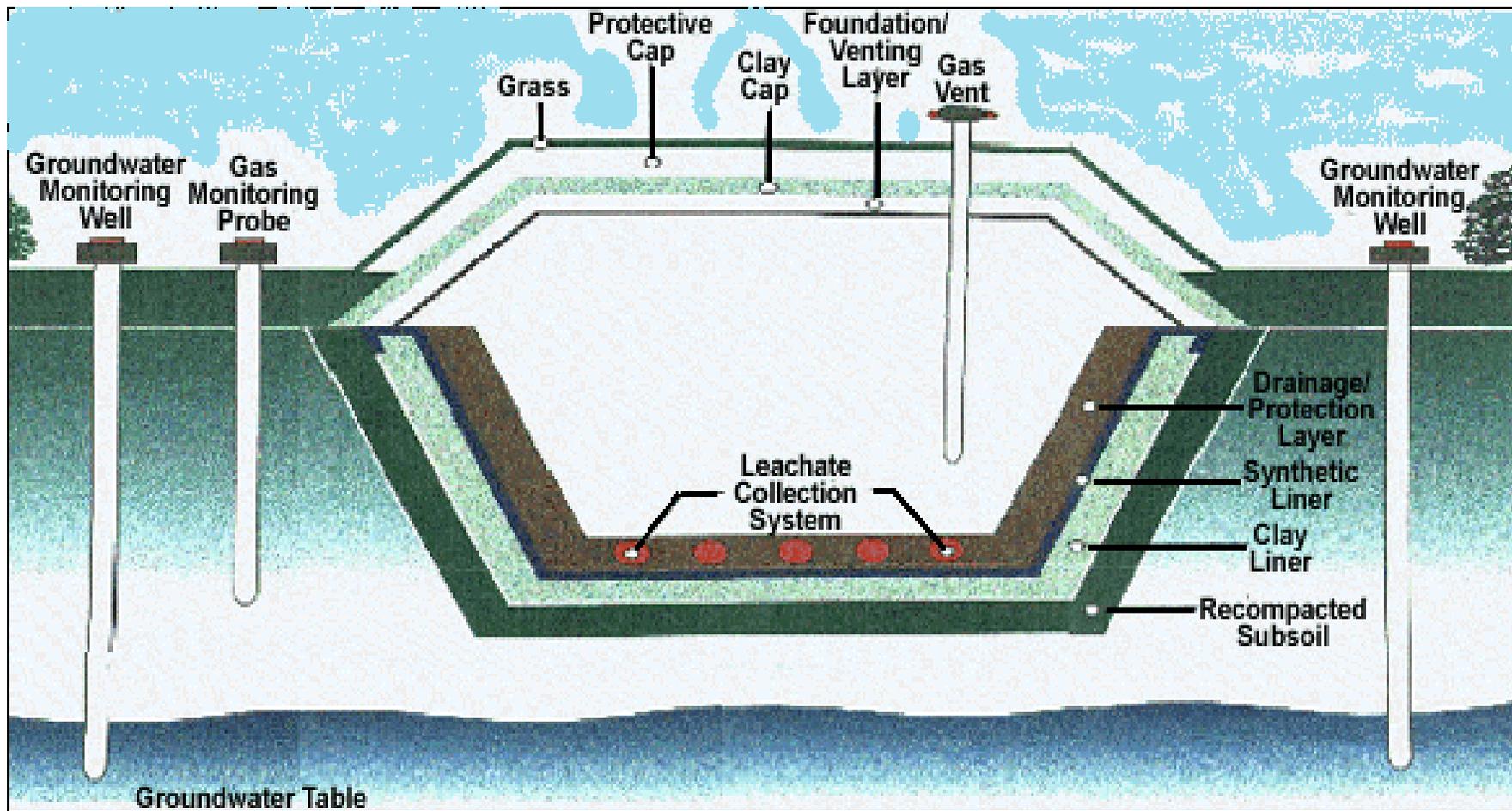


Land Disposal

- ▶ Land disposal is well proven and readily implementable
- ▶ Landfills permitted to receive hazardous wastes from off site are required to have double liners, leachate collection and leak detection systems, impermeable covers, and groundwater monitoring and release response programs. Waste acceptance criteria in the permit may restrict types of wastes disposed.
- ▶ Landfill units receiving wastes only from on-site generators or from on-site corrective/remedial actions may be required to meet all permitted facility standards, or reduced requirements depending on site- and waste-specific conditions
- ▶ Disposal units that existed prior to promulgation of permitting rules are usually left in place, unless releases have occurred



Land Disposal – Basic Landfill Components



Applicability and Limitations

- ▶ Excavation and land disposal are applicable to most contaminant groups
- ▶ Factors that may limit the applicability and effectiveness of the processes:
 - Generation of fugitive emissions may be a problem during operations
 - Depth and composition of the waste/media requiring excavation must be considered, including potential toxic exposures to workers
 - Transportation of the waste/soil through populated areas may effect community acceptability
 - Disposal options for mixed (radioactive/hazardous) and some reactive/ignitable wastes (e.g., phosphorus production sludge) are limited
 - Treatment costs may greatly exceed excavation, transport, and landfill costs
 - On-site subsurface barriers, capping, or other containment technologies may be preferable for historical waste disposal units, even where releases occurred



Data Requirements

- ▶ Factors to consider in design of an excavation project
 - Hazardous constituents that may be released during excavation/transport
 - Hazardous characteristics that may require special handling
 - Need for containerization
 - Economy of scale (e.g., small projects will have high unit costs)
 - Costs and risks of transport and treatment

- ▶ Factors to consider in the design or use of a disposal facility
 - Site location and characteristics (avoid sensitive, wet, or unstable sites)
 - Compliance status (unit should meet all RCRA design and operating criteria)
 - Transport costs, special handling of wastes, potential waste acceptance problems, added sampling and analysis costs
 - Maintenance, monitoring, and corrective action for releases at disposal sites must continue “forever.” There is permanent liability that could result in large future costs.



Performance and Cost

- ▶ The rate and cost of excavation and disposal depends on a number of factors, including:
 - Dimensions of the materials to be excavated
 - Excavation method (e.g., continuous, lift depths)
 - Type of equipment and capacity
 - Number of loaders and trucks operating; utility or exposure constraints
 - Distance(s) between excavation, treatment, and disposal sites
 - Treatment requirements to meet land disposal restrictions
 - Depth of excavation and worker safety



Performance and Cost

▶ Examples

- The excavation of 20,000 tons of contaminated soil would typically require about two months
- Costs for bulk excavation, short distance transport, and disposal may range from \$270 to \$460 per ton, not including treatment, depending on the nature of hazardous wastes and methods of excavation. Costs for wastes in containers, or for long distance transport, may be substantially higher.

Excavation Photographs



Excavation Photographs



Ex-Situ Solidification/Stabilization



Ex-Situ Solidification/Stabilization

- ▶ Solidification treatment processes change the physical characteristics of the waste to improve its handling and to reduce the mobility of the contaminants by creating a physical barrier to leaching
- ▶ Stabilization (or immobilization) treatment processes convert contaminants to less mobile forms through chemical or thermal interactions
- ▶ There are two basic types of solidification/stabilization treatments
 - Reagent
 - Thermal (or vitrification)
 - This section will focus on the reagent type



Ex-Situ Solidification/Stabilization

- ▶ The objective of solidification/stabilization treatment is to:
 - Reduce the mobility or solubility of the contaminants to levels required by regulatory or risk-based standards
 - Limit the contact between contaminants and site fluids (surface water and groundwater) by reducing permeability of the waste (generally to 10^{-6} cm/sec)
 - Increase the compression strength (>50 psi)
 - Retention of integrity when subjected to expected freeze/thaw and wet/dry cycles

- ▶ Often used as a pre-treatment for land disposal activities to meet land disposal restrictions (LDRs)



Bituminization

- ▶ Bitumen (coal tar) is a very strong and durable adhesive that binds together a wide variety of materials without effecting their properties. Its durability is essential to major engineering projects such as roads and waterways
- ▶ In bituminization, wastes are embedded in molten bitumen and encapsulated when the bitumen coals. The process combines heated bitumen and a concentrate of the waste material, usually in slurry form, in a heated extruder containing screws that mix the bitumen and waste.
- ▶ Water is evaporated from the mixture to about 0.5% moisture
- ▶ The final product is a homogenous mixture of extruded solids and bitumen



Portland Cement

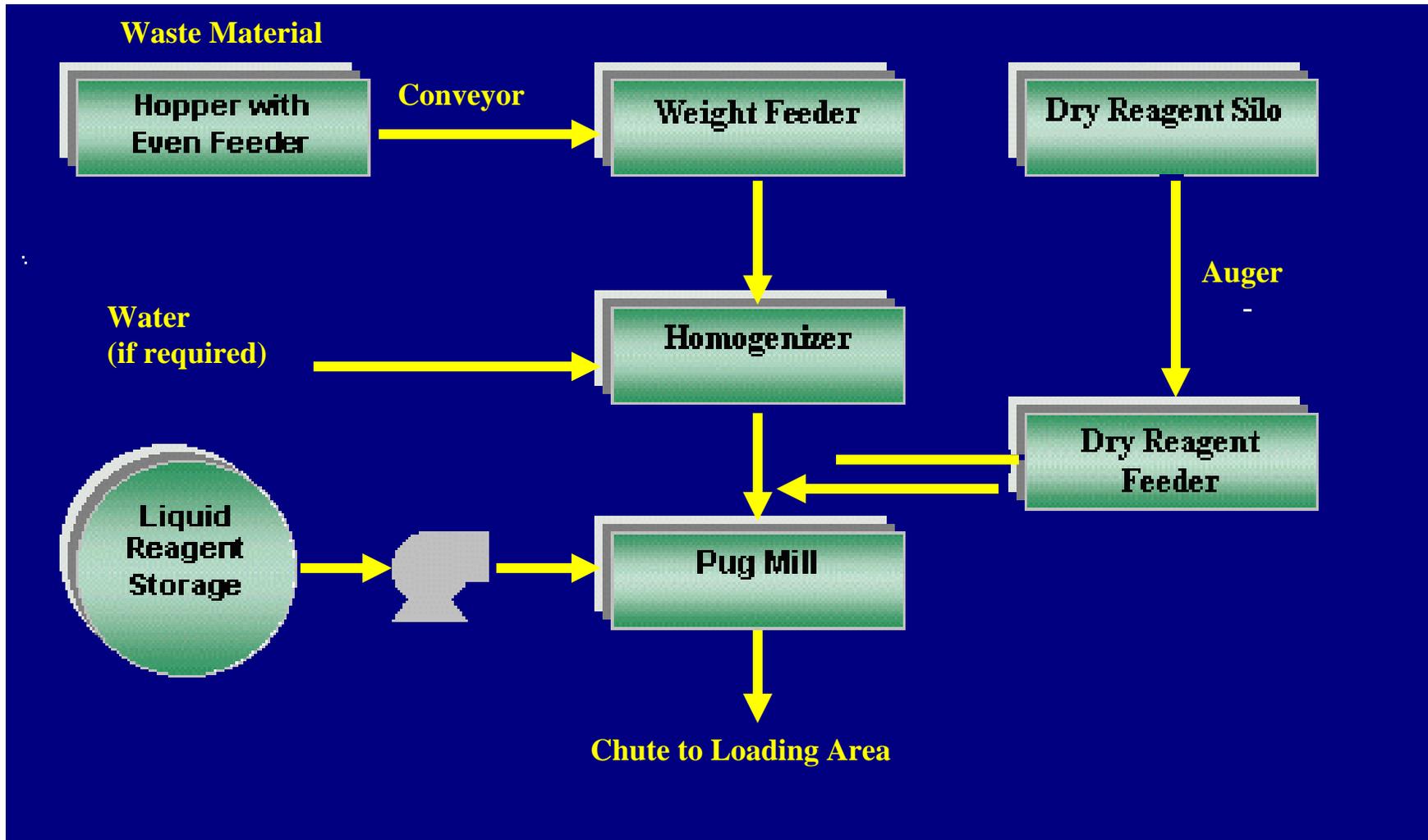
- ▶ Portland cement-based process consists of mixing the waste materials with Portland cement
- ▶ Water is added, if necessary, to ensure proper hydration reaction necessary to bond the cement
- ▶ The waste material is incorporated into the cement matrix, which improves the handling and physical characteristics of the waste
- ▶ They also raise the pH of the water, which may help precipitate and immobilize some heavy metal contaminants
- ▶ The final product varies from a granular, soil-like material to a solid depending upon the amount of reagent added and the type of waste stabilized/solidified



Pozzolanic Processes

- ▶ Pozzolanic processes consists of mixing silicates (fly ash, kiln dust, pumice, or blast furnace slag) with lime or cement and water
- ▶ These materials chemically react with water to form a solid cementitious matrix, which improves the handling and physical characteristics of the waste
- ▶ The reaction is generally much slower than the Portland cement process, which also raises the pH of the water which may help immobilize some heavy metal contaminants
- ▶ The final product varies from a soft fine-grained material to a cohesive solid similar in appearance to cement

Solidification/Stabilization Schematic



Solidification/Stabilization Equipment Pug Mill



Solidification/Stabilization Equipment Paddle Mixer (inside)



Solidification Photos (Reagent)



Applicability and Limitations

- ▶ Ex-situ solidification/stabilization is primarily applicable to inorganics, including radionuclides
- ▶ The technology has limited effectiveness for semi-volatiles, pesticides, and some organics
- ▶ Factors that may limit the applicability include:
 - Environmental conditions may affect long-term immobilization of contaminants
 - Generally not used in excavations below 15 feet
 - Some processes result in a significant increase in volume (up to double the original volume)
 - Certain wastes are incompatible with different processes
 - Treatability studies are generally required
 - Generally not effective in soils with high organic content



Data Requirements

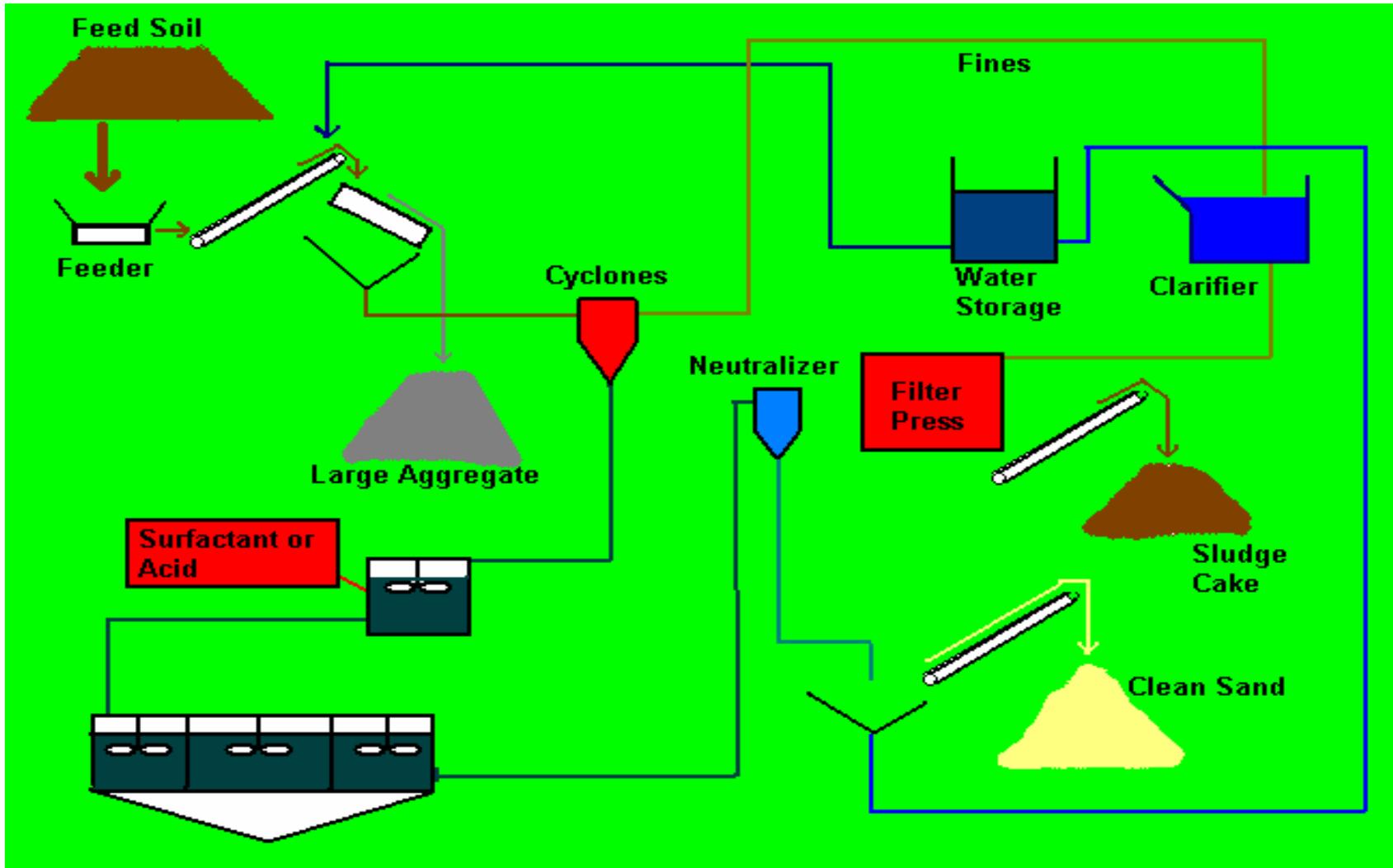
- ▶ Soil parameters that must be determined include:
 - Reagent additive ratio (from treatability study)
 - Particle size
 - Atterberg limits
 - Moisture content
 - Metal concentrations
 - Sulfate content
 - Organic content
 - Density, permeability
 - Unconfined compressive strength
 - Leachability
 - Microstructure analysis
 - Physical and chemical durability



Performance and Cost

- ▶ Ex-situ solidification/stabilization processes are among the most mature remediation technologies
- ▶ Ex-situ solidification/stabilization is a short- to medium-term technology. Long-term effectiveness has not been demonstrated for many contaminant/process combinations.
- ▶ Factors affecting cost include:
 - Type of waste
 - Density of waste
 - Total volume
 - System size (batch mix plants are typically 2, 5, 10, or 15 cubic yards)
 - Processing or reaction time
- ▶ Representative overall cost is approximately \$100 per ton, including excavation

Soil Washing



Soil Washing

- ▶ Ex-situ soil separation processes (often referred to as "soil washing"), mostly based on mineral processing techniques, are widely used for the treatment of contaminated soil

- ▶ Soil washing is a water-based process for scrubbing soils ex-situ to remove contaminants by:
 - Dissolving or suspending them in the wash solution (which can be sustained by chemical manipulation of pH for a period of time), or
 - Concentrating them into a smaller volume of soil through particle size separation, gravity separation, and attrition scrubbing (similar to those techniques used in sand and gravel operations)

Applicability

- ▶ The target contaminant groups for soil washing are semi-volatiles, fuels, and heavy metals. The technology offers the ability for recovery of metals and can clean a wide range of organic and inorganic contaminants from coarse-grained soils.
- ▶ The technology can be used on selected VOCs and pesticides
- ▶ Soil washing systems offer the greatest promise for soils contaminated with radionuclides and organic contaminants
- ▶ Commercialization of the process, however, is not yet extensive

Limitations

- ▶ Factors that may limit the applicability and effectiveness of the process include:
 - Complex waste mixtures (e.g., metals with organics) make formulating washing fluid difficult
 - High humic content in soil may require pretreatment
 - The aqueous stream will require treatment at demobilization
 - Additional treatment steps may be required to address hazardous levels of washing solvent remaining in the treated residuals
 - It may be difficult to remove organics adsorbed onto clay-size particles



Data Requirements

- ▶ The following site and soil considerations to be addressed include:
 - Particle size distribution (0.24 to 2 mm optimum range)
 - Soil type, physical form, handling properties, and moisture content
 - Contaminant type and concentration
 - Texture
 - Organic content
 - Cation exchange capacity
 - pH and buffering capacity

- ▶ A complete bench scale treatability study should always be completed before applying this technology as a remedial solution

Performance

- ▶ At the present time, soil washing is used extensively in Europe but has had limited use in the United States

- ▶ Two pilot scale demonstrations were conducted at Fort Polk, LA in 1996
 - Employed commercially available unit processes - physical separation/acid leaching systems
 - One system employed acetic acid as the leaching agent, and the other, hydrochloric acid
 - Input soil had a lead content of approximately 3,500 mg/kg
 - The hydrochloric acid system was most effective
 - Processed soil had total lead concentration of 200 mg/kg and TCLP levels for lead of approximately 2 mg/L
 - The throughput rate was approximately six tons per hour



Cost

- ▶ The average cost for use of this technology, including excavation, is approximately \$170 per ton, depending on site-specific conditions and the target waste quantity and concentration

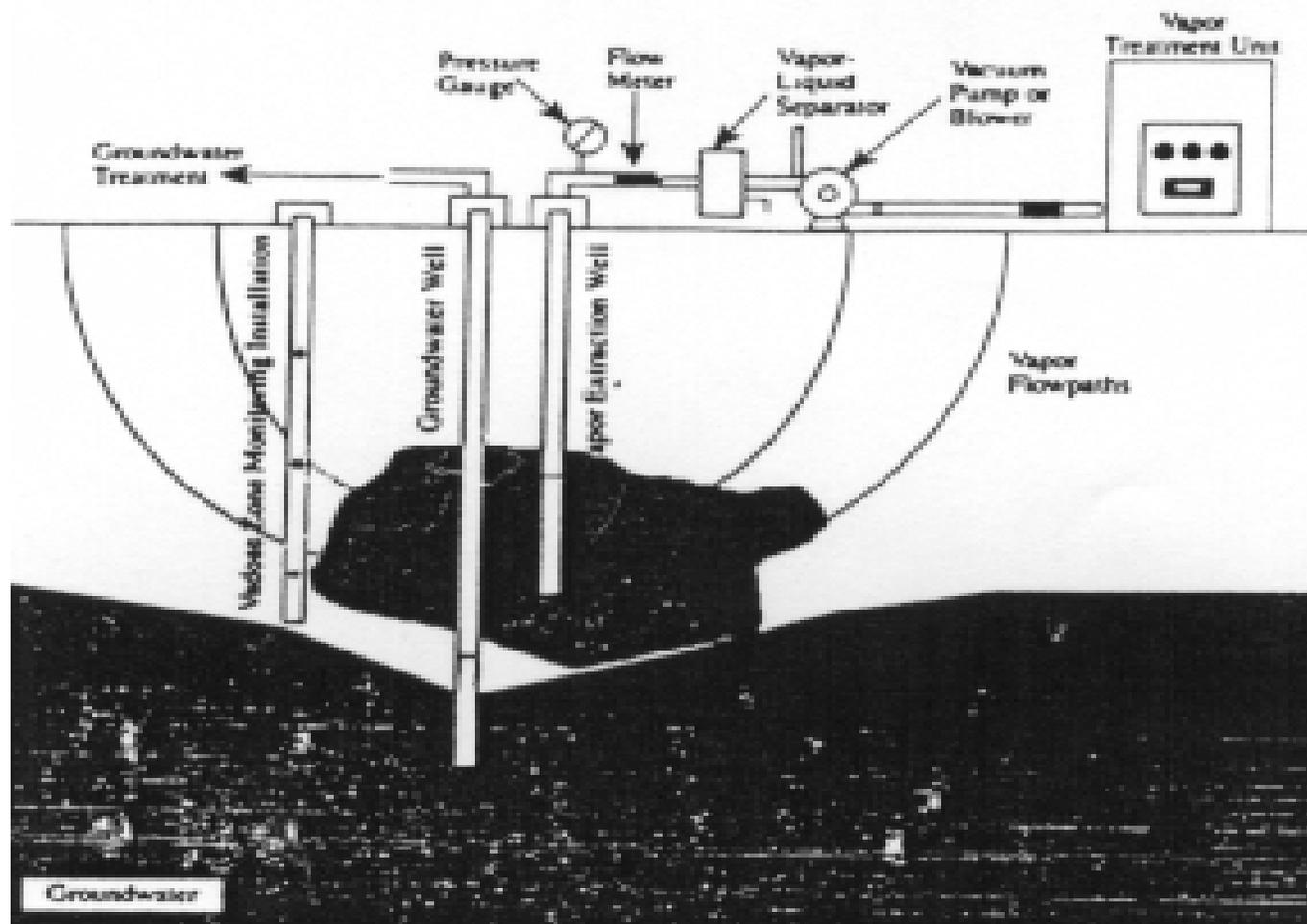
Soil Washing Process



In-situ Soil Treatment Processes



Soil Vapor Extraction



Soil Vapor Extraction (SVE)

- ▶ Soil vapor extraction (SVE) extracts soil vapor from the unsaturated zone, utilizing blowers or vacuum pumps to draw air through the contaminated material
- ▶ Airflow is induced by creating a pressure gradient in the soil, thereby enhancing evaporation, volatilization, and desorption of contaminants from the soil
- ▶ SVE typically requires one or more extraction wells installed in the unsaturated zone
- ▶ Accouterments may include air injection wells, low permeability caps, air/water separators, and off-gas treatment

Soil Vapor Extraction (SVE)

- ▶ One of the most often and widely used remediation technologies today
- ▶ One of the most efficient and cost effective means to remove VOCs from unsaturated soil
- ▶ Flexible/adaptable and can be used under many conditions
- ▶ Is often used in conjunction with other technologies to achieve the intended results (e.g., bioventing, sparging, dual-phase recovery, in-situ heating, steam injection, pump and treat, and fracturing)

Limitations

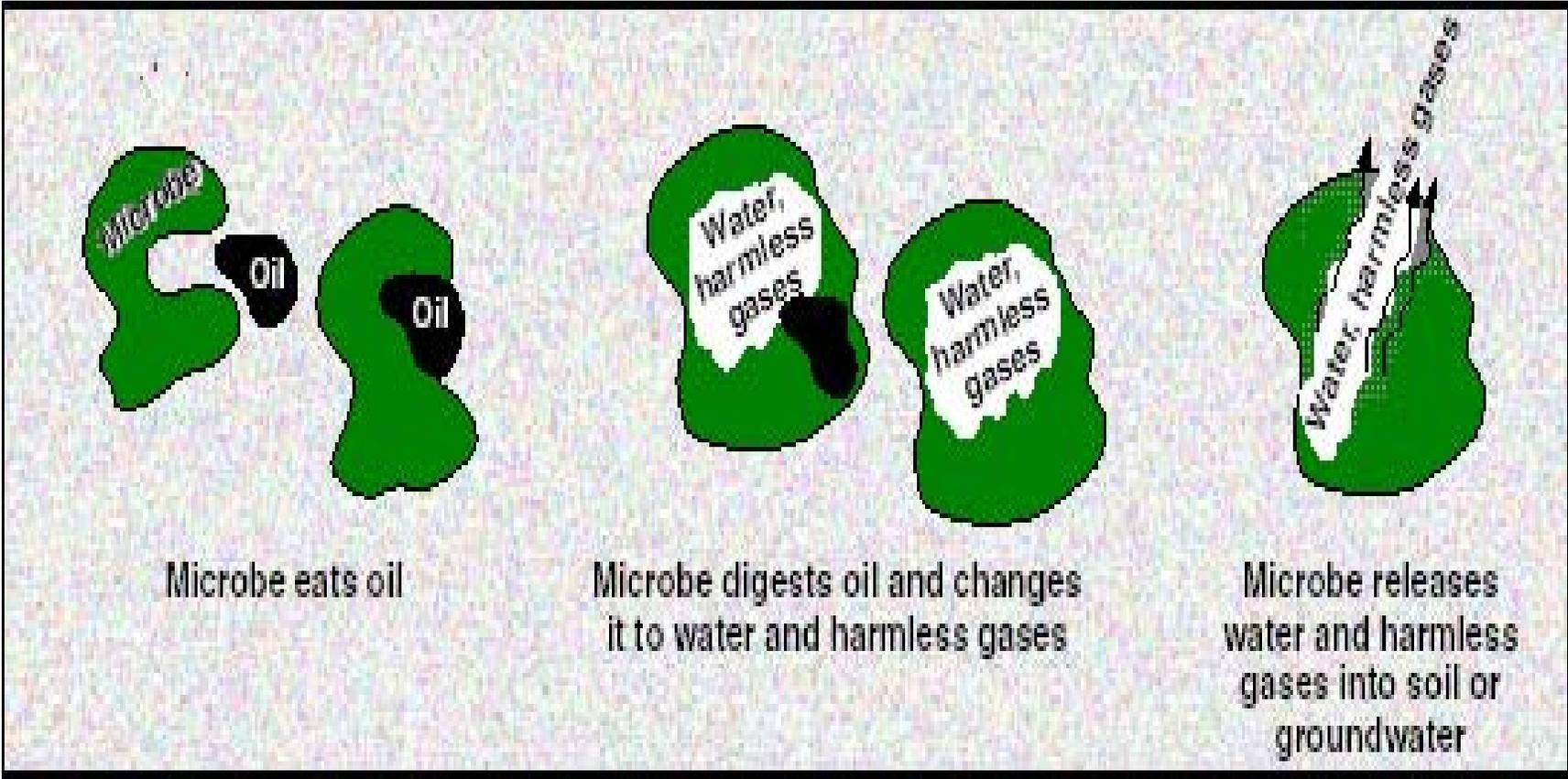
- ▶ Soil must be permeable to air ($> 10^{-8} \text{ cm}^2$)
- ▶ Does not extract SVOCs (vapor pressure $< 0.5 \text{ mm Hg @} 20^\circ\text{C}$, see Bioventing)
- ▶ Off-gas treatment costs can be high
- ▶ Cannot overcome inadequate characterization or design
- ▶ Shallow groundwater table

Performance

- ▶ The duration of SVE can range from several months to several years

- ▶ Factors that affect duration:
 - Soil and contaminant properties
 - Size of zone being treated
 - Rate of air exchange
 - Performance of combined technologies
 - Adequacy of monitoring

Bioremediation



Bioremediation

- ▶ Bioremediation is a process in which indigenous or inoculated microorganisms that live in soil or groundwater (e.g., fungi, bacteria) degrade (i.e., metabolize) organic contaminants, such as gasoline and oil, in soil and/or groundwater
- ▶ These microscopic “bugs” or microbes will digest the contaminants and convert them to harmless end products, such as carbon dioxide
- ▶ Nutrients, oxygen, or other amendments are used to enhance the ability of native microorganisms to degrade these contaminants
- ▶ Two classes of bioremediation are:
 - Aerobic
 - Anaerobic

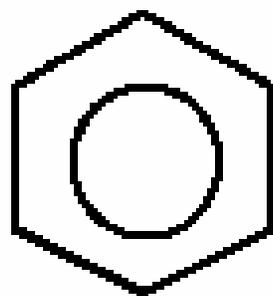


Aerobic Bioremediation

- ▶ Under aerobic conditions, and with proper nutrient elements, microorganisms will convert many organic contaminants to carbon dioxide, water, and microbial cell mass
 - Enhanced bioremediation of soil typically involves the percolation or injection of groundwater or uncontaminated water mixed with nutrients and saturated with dissolved oxygen
 - An infiltration gallery or spray irrigation is typically used for shallow contaminated soils, and injection wells are used for deeper contaminated soils
 - Although successful in-situ bioremediation has been demonstrated in cold weather climates, low temperature slows the remediation process
 - Heat blankets may be used to cover the soil surface to increase the soil temperature and degradation rate

Aerobic Bioremediation

Aerobic Biodegradation



Benzene



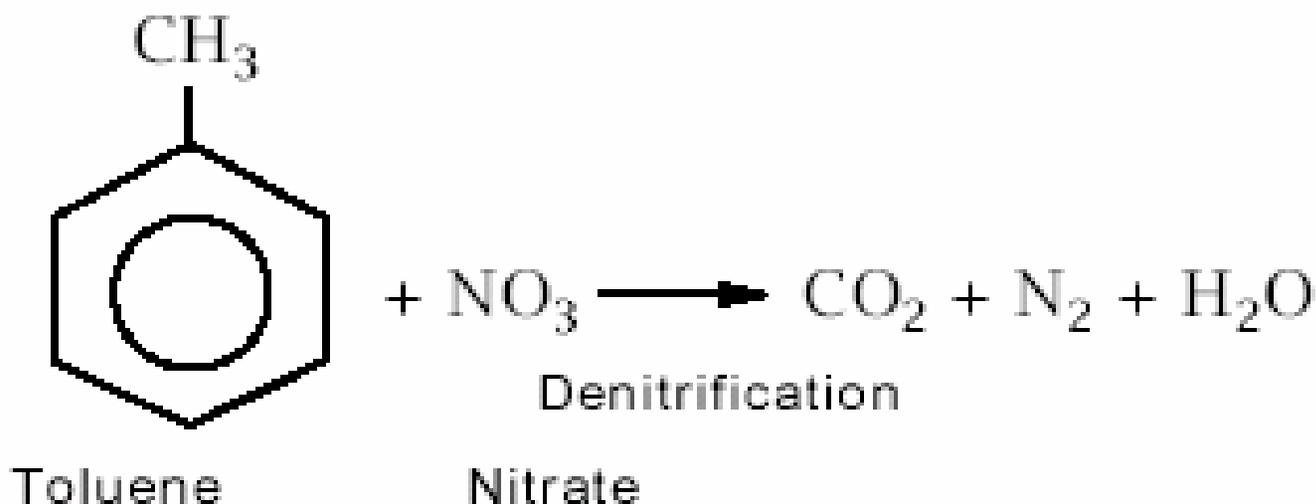
Anaerobic Bioremediation

- ▶ Under anaerobic conditions, organic contaminants will be ultimately metabolized to methane, limited amounts of carbon dioxide, and trace amounts of hydrogen gas
- ▶ Under sulfate-reduction conditions, sulfate is converted to sulfide or elemental sulfur, and under nitrate-reduction conditions, di-nitrogen gas is ultimately produced
- ▶ Sometimes contaminants may be degraded to intermediate or final products that may be less, equally, or more hazardous than the original contaminant
 - TCE anaerobically biodegrades to the persistent and more toxic vinyl chloride. To avoid such problems, most bioremediation projects are conducted in situ. Vinyl chloride has been shown to be easily broken down further to ethene if aerobic conditions are created.



Anaerobic Bioremediation

Anaerobic Biodegradation



Applicability

- ▶ Bioremediation techniques have been successfully used to remediate soils, sludges, and groundwater contaminated with petroleum hydrocarbons, solvents, pesticides, wood preservatives, and other organic chemicals
 - Bench- and pilot-scale studies have demonstrated the effectiveness of anaerobic microbial degradation of nitrotoluenes in soil
 - Bioremediation is especially effective for remediating low-level residual contamination in conjunction with source removal
 - The contaminant groups treated most often are PAHs, non-halogenated SVOCs, and BTEX

- ▶ Bioremediation cannot degrade inorganic contaminants but can be used to change the valence state of inorganics and cause adsorption, immobilization onto soil particulates, precipitation, uptake, and accumulation



Limitations

- ▶ Soil matrix may prohibit contaminant-microorganism contact
- ▶ The circulation of water-based solutions through the soil may increase contaminant mobility and necessitate treatment of underlying groundwater
- ▶ Preferential colonization by microbes may occur causing clogging of nutrient and water injection wells
- ▶ The system should not be used for clay, highly layered, or heterogeneous subsurface environments because of oxygen transfer limitations
- ▶ High concentrations of heavy metals, highly chlorinated organics, long chain hydrocarbons, or inorganic salts are likely to be toxic to microorganisms
- ▶ Bioremediation slows at low temperatures
- ▶ Hydrogen peroxide concentration >100 to 200 ppm in groundwater inhibit the activity of microorganisms
- ▶ A surface treatment system, such as air stripping or carbon adsorption, may be required to treat extracted groundwater prior to re-injection or disposal

Data Requirements

- ▶ Soil characteristics:
 - Oxygen: Oxygen must be present in the soil for aerobic degradation or can be supplied via a piping network. Oxygen levels should be maintained above 15% in the soil.
 - Water: Water is essential for microbial activity, but too much can block the soil pores and restrict airflow. Soil moisture should be maintained at 70 to 95% of the soil capacity.
 - Nutrients: Nitrogen, phosphorous, sulfur, magnesium, calcium, manganese, iron, zinc, and copper are essential nutrients for microbial activity. Nitrogen and phosphorous are nutrients of concern in hydrocarbon impacted soil.
 - pH: Most hydrocarbon bacteria grow best at a neutral to slightly alkaline pH, primarily within the 5.5 to 8.5 range.
 - Temperature: Optimal temperature for microbial activity ranges from 50 to 100 °F.
 - Microbial Population: Typically, the indigenous microbial population is sufficient to bioremediate contamination.



Data Requirements (cont.)

- ▶ Contaminant characteristics:
 - Leaching potential (e.g., water solubility and soil sorption coefficient)
 - Chemical reactivity (e.g., tendency toward nonbiological reactions, such as hydrolysis, oxidation, and polymerization)
 - Biodegradability

- ▶ Treatability or feasibility tests are performed to determine whether enhanced bioremediation is feasible in a given situation, and to define the remediation time frame and parameters

- ▶ Field testing can be performed to determine the radius of influence and well spacing and to obtain preliminary cost estimates

Cost

- ▶ Typical remediation costs for bioremediation range from \$25 to \$70 per ton of soil

- ▶ Factors that affect cost include:
 - Amount and type of soil
 - Type and quantity of amendments used
 - Type and level of contamination
 - Climatic conditions
 - Site restrictions
 - Regulatory requirements

